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13. ABSTRACT (Maximum 200 words)  The known bis(bis(trimethylsilyl)amino)alane $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\mu\text{-H})\}_2$ ( <b>1</b> ) is obtained from disproportionation of the base-stabilized monomeric bis(trimethylsilyl)aminoalane $[(\text{Me}_3\text{Si})_2\text{NAlH}_2]\cdot\text{NMe}_3$ in refluxing toluene. The single-crystal X-ray structure determination for <b>1</b> provides a H-bridged planar dimer with exo-cyclic $\text{N}(\text{SiMe}_3)_2$ groups. The combination of <b>1</b> with $\text{HNMe}_2$ in a 1:1 ratio results in competing aminolysis at the Al-H site and transamination at the Al-N( $\text{SiMe}_3$ ) <sub>2</sub> site of <b>1</b> , as illustrated by the molecular structure of $(\text{Me}_3\text{Si})_2\text{N}(\text{Me}_2\text{N})\text{Al}(\mu\text{-NMe}_2)_2\text{Al}(\text{H})\text{N}(\text{SiMe}_3)_2$ ( <b>2</b> ) which is isolated from this system. The characteristic structural feature of <b>2</b> is a puckered {Al-N-Al-N} ring with different ligands on two aluminum atoms.				
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**N-Bridged and H-Bridged Aminoalanes: Single-Crystal X-ray Structure Determinations for the Planar Dimer  $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\mu\text{-H})\}_2$  and the Puckered Four-Membered Ring Compound  $(\text{Me}_3\text{Si})_2\text{N}(\text{Me}_2\text{N})\text{Al}(\mu\text{-NMe}_2)_2\text{Al}(\text{H})\text{N}(\text{SiMe}_3)_2$ .**

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**Abstract:** The known bis(bis(trimethylsilyl)amino)alane  $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\mu\text{-H})\}_2$  (**1**) is obtained from disproportionation of the base-stabilized monomeric bis(trimethylsilyl)aminoalane  $[(\text{Me}_3\text{Si})_2\text{NAlH}_2]\cdot\text{NMe}_3$  in refluxing toluene. The single-crystal X-ray structure determination for **1** provides a H-bridged planar dimer with exocyclic  $\text{N}(\text{SiMe}_3)_2$  groups. The combination of **1** with  $\text{HNMe}_2$  in a 1:1 ratio results in competing aminolysis at the Al-H site and transamination at the Al-N( $\text{SiMe}_3$ )<sub>2</sub> site of **1**, as illustrated by the molecular structure of  $(\text{Me}_3\text{Si})_2\text{N}(\text{Me}_2\text{N})\text{Al}(\mu\text{-NMe}_2)_2\text{Al}(\text{H})\text{N}(\text{SiMe}_3)_2$  (**2**) which is isolated from this system. The characteristic structural feature of **2** is a puckered {Al-N-Al-N} ring with different ligands on two aluminum atoms.

**Keywords:** alanes; trimethylsilylamines; disproportionation; transamination; aminolysis; precursors.

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## Introduction

In the solid state, some alane amine adducts show dimeric connectivities  $[\text{H}_3\text{Al}\cdot\text{L}]_2$  (for example,  $\text{L} = \text{NMe}_3$ ,<sup>1a</sup>  $\text{NMe}_2\text{CH}_2\text{Ph}$ <sup>1b</sup>) with five-coordinated aluminum atoms and somewhat counterintuitive unsymmetrical Al–H–Al bridges while, on the other hand, others seem to favor a monomeric mode with four-coordinated Al in  $\text{H}_3\text{Al}\cdot\text{L}$  (for example,  $\text{L} = \text{N}(\text{n-Bu})_3$ <sup>1c</sup>, quinuclidine<sup>1d</sup>) or five-coordinated Al having a N–Al(H<sub>3</sub>)–N bond sequence as in trigonal bipyramidal  $\text{H}_3\text{Al}\cdot 2\text{NMe}_3$ .<sup>1e</sup> This span of bonding preferences in the alane adducts is generally interpreted as a manifestation of the ligand's steric hindrance and is not an exclusive property of amine Lewis bases. The latter is illustrated by examples of the Al–H–Al bridged dimer  $[\text{H}_3\text{Al}\cdot\text{THF}]_2$  and trigonal bipyramidal  $\text{H}_3\text{Al}\cdot 2\text{THF}$  with an O–Al(H<sub>3</sub>)–O axis.<sup>1f</sup> Even more complex bonding environments are encountered in some polymeric structures containing  $\text{AlH}_3$  units.<sup>1g</sup> Finally, ionic bonding is displayed by rare species of the type  $(\text{H}_2\text{AlL})^+(\text{AlH}_4)^-$  where L is a tri- or tetradentate amine ligand.<sup>1h</sup> The progress in the chemistry of Lewis base adducts of alane and gallane has recently been reviewed.<sup>1i</sup>

The aminoalanes,  $\{\text{H}_n\text{Al}(\text{NR}_2)_{3-n}\}$  ( $n = 0, 1, 2$ ), appear to exhibit similar diversity of bonding as outlined above for alane amine adducts but relatively shorter Al–N bond lengths in the former make the steric factor play a more obvious role. For example, the dimethylaminoalane,  $(\text{H}_2\text{AlNMe}_2)_3$ , is a N-bridged trimer in solution<sup>2a</sup> and in the solid state<sup>2b</sup> but both bis(dimethylamino)alane,  $[\text{HAl}(\text{NMe}_2)_2]_2$ ,<sup>2c</sup> and tris(dimethylamino)alane,  $[\text{Al}(\text{NMe}_2)_3]_2$ ,<sup>2d, e</sup> are N-bridged dimers. Even larger  $\text{NR}_2$  groups may result in N-bridged dimeric cores such as found in 2,6-dimethylpiperidinoalane,  $[\text{H}_2\text{Al}(\text{dmp})]_2$ .<sup>2f</sup> A further increase of the bulkiness of the piperidino ligand, in the absence of  $\text{NMe}_3$  as in the reaction between  $\text{LiAlH}_4$  with  $(\text{tmpH})\cdot\text{HCl}$ , yields a postulated H-bridged trimer 2,2,6,6-tetramethylpiperidinoalane,  $[\text{H}_2\text{Al}(\text{tmp})]_3$ , or, even in the presence of  $\text{NMe}_3$  in the reaction between  $\text{H}_3\text{Al}\cdot\text{NMe}_3$  with 2 equivalents of tmpH, gives the authenticated H-bridged dimer

bis(2,2,6,6-tetramethylpiperidino)alane,  $[\text{HAl}(\text{tmp})_2]_2$ .<sup>2f</sup> On the other hand, an extreme bulkiness of  $\text{N}(\text{SiMe}_3)_2$  coupled with a latent N-basicity in this group is thought to be responsible for the kinetic stabilization of the unassociated  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ .<sup>2g</sup>

In addition to the formation of the N- or H-bridged aminoalanes, stabilization of the aminoalane unit by an available Lewis base may sometimes also be favorable. In systems utilizing the convenient form of alane,  $\text{H}_3\text{Al}\cdot\text{NMe}_3$ , trimethylamine as a potent Lewis base is found in a few cases to play that role. It was originally reported that the monomeric aminoalane, stabilized by coordination of  $\text{NMe}_3$  at the Al-site,  $[\text{H}_2\text{AlN}(\text{SiMe}_3)_2]\cdot\text{NMe}_3$ , was formed from the reaction between  $\text{H}_3\text{Al}\cdot\text{NMe}_3$  and  $\text{HN}(\text{SiMe}_3)_2$ .<sup>3</sup> This finding was later confirmed in a parallel study, which additionally provided a structural proof for a related  $[\text{H}(\text{Cl})\text{AlN}(\text{SiMe}_3)_2]\cdot\text{NMe}_3$ .<sup>4a</sup> Further, a 1:1 ratio reaction between  $\text{H}_3\text{Al}\cdot\text{NMe}_3$  and  $\text{tmpH}$  afforded  $[\text{H}_2\text{Al}(\text{tmp})]\cdot\text{NMe}_3$ ,<sup>4b</sup> which can be compared with the previously discussed H-bridged trimer  $[\text{H}_2\text{Al}(\text{tmp})]_3$ .<sup>2f</sup> obtained in the absence of trimethylamine. One should be aware that this kind of adduct stabilization extends into other group 3–5 systems and, for example, is also found in the pnictinoalanes  $[\text{H}_2\text{AlE}(\text{Mes})_2]\cdot\text{NMe}_3$  ( $\text{E} = \text{P}, \text{As}$ )<sup>4c</sup> and  $[\text{H}_2\text{AlAs}(\text{SiMe}_3)_2]\cdot\text{NMe}_3$ .<sup>4d</sup>

The original reports by Paine and coworkers on the preparation of  $[\text{H}_2\text{AlN}(\text{SiMe}_3)_2]\cdot\text{NMe}_3$ <sup>3</sup> indicated that thermal decomposition of this compound resulted in the formation of new bis(bis(trimethylsilyl)amino)alane  $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\mu\text{-H})\}_n$  of an undetermined degree of oligomerization; some analytical evidence, however, supported the presence of Al–H–Al bridges in this product.<sup>3b</sup> This was contrary to what the parallel report by Raston and coworkers claimed about the thermal behavior of  $[\text{H}_2\text{AlN}(\text{SiMe}_3)_2]\cdot\text{NMe}_3$ ,<sup>4a</sup> namely, decomposition to elemental aluminum presumably along a reductive coupling pathway with dihydrogen evolution and, here, additionally, with concurrent release of  $\text{NMe}_3$ . In this regard, one has to be aware that reductive coupling is not the only thermally induced decomposition pathway for aminoalanes and it has long been known that their ligand disproportionation chemistry is of equal importance.<sup>2c, 5</sup>

Herein, we confirm the originally reported disproportionation of  $[\text{H}_2\text{AlN}(\text{SiMe}_3)_2]\cdot\text{NMe}_3$  and describe the single-crystal X-ray diffraction study for the resulting H-bridged dimer, bis(bis(trimethylsilyl)amino)alane  $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\mu\text{-H})\}_2$  (**1**). We also outline the reaction of **1** with  $\text{HNMe}_2$  and the isolation of an unsymmetrically substituted product  $(\text{Me}_3\text{Si})_2\text{N}(\text{Me}_2\text{N})\text{Al}(\mu\text{-NMe}_2)_2\text{Al}(\text{H})\text{N}(\text{SiMe}_3)_2$  (**2**) for which a single-crystal structure is presented.

## Experimental

**General techniques.** All experiments were carried out using standard vacuum/Schlenk techniques. Solvents were dried and distilled from Na benzophenone ketyl or Na/K alloy prior to use.  $\text{HNMe}_2$  was obtained from Aldrich and used as received.  $[\text{H}_2\text{AlN}(\text{SiMe}_3)_2]\cdot\text{NMe}_3$  and  $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\mu\text{-H})\}_2$  were prepared by the literature methods;<sup>3b</sup> the synthesis and characterization of the latter is also described in more detail below.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were acquired on the Varian Unity 400 spectrometer at 25 °C from toluene- $d_8$  solutions and referenced vs  $\text{SiMe}_4$  by generally accepted methods. Mass spectra were collected on a JEOL JMS-SX 102A spectrometer operating in the EI mode at 20 eV. IR spectra of solids and oily products were acquired using KBr pellets and NaCl plates, respectively, on a BOMEM Michelson MB-100 FT-IR spectrometer. A calibrated manifold was used for volume estimations of reaction gases. Melting behavior (uncorrected) was determined with a Thomas-Hoover Uni-melt apparatus for samples flame-sealed in glass capillaries. Single-crystal X-ray diffraction studies for **1** and **2** were performed at the University of Delaware, Department of Chemistry and Biochemistry, Newark, DE, on a Siemens P4/CCD diffractometer, using  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). All calculations were carried out with the help of SHELXTL 5.03 programs;<sup>6</sup> the structures were solved by direct methods.

**Preparation of  $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\mu\text{-H})\}_2$  (2).** A sample of  $[\text{H}_2\text{AlN}(\text{SiMe}_3)_2]\cdot\text{NMe}_3$ , 1.24 g or 5.0 mmol, was dissolved in about 10–15 mL of toluene, stirred, and refluxed overnight under nitrogen. Typically, elemental aluminum precipitated on the sides of reaction flask in the form of agglomerates but, sometimes, aluminum would form as a colloidal suspension. The mixture was concentrated by evacuation to about 5–10 mL and refluxed for additional 24 hours. Subsequently, it was filtered, the volatiles evacuated from the filtrate, and the resulting residue dissolved in a few mL of hexane. The concentrated hexane solution after storage at  $-30\text{ }^\circ\text{C}$  afforded abundant colorless crystals of **1**, 0.48g or 55% yield based on equation 1 (*vide infra*). More crystalline product could be recovered from the solution by further concentrating and repeating the low temperature crystallization. M.p.  $95\text{--}97\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR:  $\delta$  0.34 (36H;  $\text{SiMe}_3$ ), 4.4 (1H, br; AlH).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  6.0 ( $\text{SiMe}_3$ ). MS: m/e (intensity) (ion): peak clusters around: 695 (1) ( $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\mu\text{-H})\}_2 - \text{H}$  or  $\text{M} - \text{H}$ ), 667 (1) ( $\text{M} - 2\text{Me} + \text{H}$ ), 596 (1) ( $\text{M} - \text{SiMe}_3 + 3\text{H}$ ), 552 (2) ( $\text{M} - 2\text{SiMe}_3 + 2\text{H}$ ), 536 (2) ( $\text{M} - \text{N}(\text{SiMe}_3)_2$ ), 492 (3) ( $\text{M} - \text{N}(\text{SiMe}_3)_2 - 3\text{Me} + \text{H}$ ), 461 (2) ( $\text{M} - \text{N}(\text{SiMe}_3)_2 - 5\text{Me}$ ) 421 (5) ( $\text{M} - \text{N}(\text{SiMe}_3)_2 - \text{SiMe}_3 - 3\text{Me} + 3\text{H}$ ), 347 (3) ( $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlH} - \text{H}$  or  $\text{M}^* - \text{H}$ ), 331 (2) ( $\text{M}^* - \text{Me} - 2\text{H}$ ), 300 (2) ( $\text{M}^* - 3\text{Me} - 3\text{H}$ ), 275 (3) ( $\text{M}^* - \text{SiMe}_3$ ), 202 (3) ( $\text{M}^* - 2\text{SiMe}_3$ ), 161 (20) ( $\text{HN}(\text{SiMe}_3)_2$ ), 146 (100) ( $\text{HN}(\text{SiMe}_3)_2 - \text{Me}$ ), 130 (10) ( $\text{HN}(\text{SiMe}_3)_2 - 2\text{Me} - \text{H}$ ), 74 (9) ( $\text{HSiMe}_3$ ). IR (KBr pellet/Nujol mull):  $\nu(\text{Al-H})$  range,  $1882/1880\text{ cm}^{-1}$ . We note that these Al–H stretching frequencies significantly differ from that of a weak band at  $1790\text{ cm}^{-1}$  originally reported for **1**.<sup>3b</sup> In the present study, the medium intensity band at about  $1880\text{ cm}^{-1}$  was reproducible, but its intensity was decreasing fast in the course of measurements due to deterioration of the sample. At this point, we are inclined to think that the band reported earlier might have been recorded for a significantly decayed sample.

**Reactions of  $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\mu\text{-H})\}_2$  with  $\text{HNMe}_2$ . Isolation of  $(\text{Me}_3\text{Si})_2\text{N}(\text{Me}_2\text{N})\text{Al}(\mu\text{-NMe}_2)_2\text{Al}(\text{H})\text{N}(\text{SiMe}_3)_2$  (2).** 0.10 g of **1** (0.14 mmol) was dissolved in about 10 mL of toluene and the reaction flask was freeze-pump-thawed three times. Onto this, using a calibrated vacuum line, 0.29 mmol of  $\text{HNMe}_2$  was deposited at  $-78\text{ }^\circ\text{C}$ . The mixture was stirred at room temperature overnight and non-condensables,  $\text{H}_2$ , were measured, 0.04 mmol. The solution was then stored for a few days at  $-30\text{ }^\circ\text{C}$ . At the end of this period, the volatiles were removed yielding an oil/solid product. IR (neat): weak to medium band in the  $\nu(\text{N-H})$  range at  $3310\text{ cm}^{-1}$ ; medium band in the  $\nu(\text{Al-H})$  range at  $1833\text{ cm}^{-1}$ . A toluene- $d_8$  NMR sample of this product was run immediately, one day, two weeks, and seven weeks after preparation. Immediately:  $^1\text{H}$  NMR (intensity) (group assignment):  $\text{SiMe}_3$  region:  $\delta$  0.08 (9) ( $\text{HN}(\text{SiMe}_3)_2$ ), 0.27 (23), 0.31 (24), 0.33 (100);  $\text{NMe}_2$  region:  $\delta$  1.88 (9), 1.89 (9), and several small intensity peaks ( $< 1$ ) in this region at 2.29, 2.32, 2.41, 2.42, 2.51, 2.60, 2.76;  $\text{AlH}$  region:  $\delta$  4.0 (very broad), 4.51.  $^{13}\text{C}\{^1\text{H}\}$  NMR (intensity) (group assignment):  $\text{SiMe}_3$  region:  $\delta$  2.6 (7) ( $\text{HN}(\text{SiMe}_3)_2$ ), 5.0 (3), 6.2 (100), 6.5 (16), 6.8 (4);  $\text{NMe}_2$  region:  $\delta$  37.9 (24), 40.4 (1), 41.6 (2), 42.0 (3), 43.2 (2), 43.5 (7). One day after:  $^1\text{H}$  NMR (intensity) (group assignment):  $\text{SiMe}_3$  region:  $\delta$  0.08 (100) ( $\text{HN}(\text{SiMe}_3)_2$ ), 0.27 (50), 0.31 (80), 0.33 (35);  $\text{NMe}_2$  region:  $\delta$  1.88 (1), 1.89 (1), 2.42 (15), 2.51 (1), 2.60 (8), 2.76 (2); no unequivocally measurable broad feature in the  $\text{AlH}$  region except for the sharp resonance at  $\delta$  4.51.  $^{13}\text{C}\{^1\text{H}\}$  NMR (intensity) (group assignment):  $\text{SiMe}_3$  region:  $\delta$  2.6 (90) ( $\text{HN}(\text{SiMe}_3)_2$ ), 4.9 (55), 6.2 (70), 6.5 (100), 6.8 (14);  $\text{NMe}_2$  region:  $\delta$  37.9 (13), 40.4 (15), 41.6 (5), 42.0 (10), 43.2 (10), 43.5 (70). Two weeks after:  $^1\text{H}$  NMR (intensity) (group assignment):  $\text{SiMe}_3$  region:  $\delta$  0.08 (100) ( $\text{HN}(\text{SiMe}_3)_2$ ), 0.27 (55), 0.31 (83), 0.33 (6);  $\text{NMe}_2$  region:  $\delta$  1.88 (1), 1.89 (1), 2.42 (16), 2.52 (3), 2.60 (8), 2.76 (4);  $\text{AlH}$  region:  $\delta$  4.1 (broad), 4.51.  $^{13}\text{C}\{^1\text{H}\}$  NMR (intensity) (group assignment):  $\text{SiMe}_3$  region:  $\delta$  2.6 (83) ( $\text{HN}(\text{SiMe}_3)_2$ ), 4.9 (63), 6.2 (35), 6.5 (100), 6.8 (32);  $\text{NMe}_2$  region:  $\delta$  37.9 (1), 40.4 (20), 41.6 (16), 42.0 (19), 43.2 (17), 43.5 (65). Seven weeks after: the NMR

spectra were identical to those obtained after two weeks. The oily/solid product was redissolved in a small amount of toluene and, subsequently, volatiles were allowed to evaporate at  $-30\text{ }^{\circ}\text{C}$  in the course of several days. After almost complete removal of volatiles, a small quantity of a colorless crystalline product was isolated. A single-crystal X-ray structure determination provided  $(\text{Me}_3\text{Si})_2\text{N}(\text{Me}_2\text{N})\text{Al}(\mu\text{-NMe}_2)_2\text{Al}(\text{H})\text{N}(\text{SiMe}_3)_2$  (**2**).  $^1\text{H}$  NMR for a freshly prepared sample (intensity) (group assignment):  $\text{SiMe}_3$  region: 0.281 (85), 0.284 (100), 0.29 (63), 0.30 (77), 0.31 (52), 0.32 (71), 0.33 (58);  $\text{NMe}_2$  region:  $\delta$  2.42 (14), 2.52 (12), 2.66 (25), 2.77 (19), 2.78 (16);  $\text{AlH}$  region: no discernible feature between  $\delta$  3.0–5.0. This sample was also run two days after preparation and showed an even more complex spectrum indicating continuing changes in the solution. IR (KBr pellet):  $\nu(\text{Al-H})$  range, medium to strong band at  $1860\text{ cm}^{-1}$ .

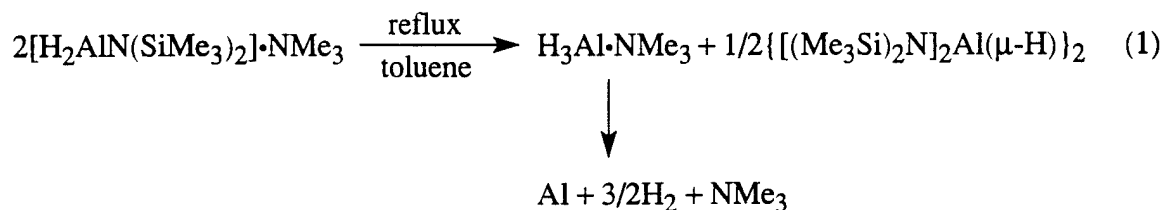
### Structural determinations for **1** and **2**.

Specimens of **1** were obtained in the form of thin colorless needles from recrystallization in toluene at  $-30\text{ }^{\circ}\text{C}$  and mounted in capillaries prior to determination. The systematic absences in the diffraction data were consistent with monoclinic space groups  $\text{P}2_1/\text{m}$  and  $\text{P}2_1$  but only the latter yielded computationally stable results and refinement. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-square procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All C-hydrogen atoms were treated as idealized contributions. The Al-hydrogen atoms were located from the difference map and were refined with fixed thermal parameters and fixed Al-H distances,  $1.727(1)\text{ \AA}$ . The geometry of the  $\{\text{Al-H-Al-H}\}$  ring was not constrained. There are two symmetry independent, but chemically similar, molecules in the asymmetric unit and the thermal ellipsoid diagram of molecule **1** is shown in Figure 1. The thermal ellipsoid diagram of molecule **2** is available in the Supporting Information. Specimens of **2** were obtained as blocky colorless crystals from slow evaporation of toluene at  $-30\text{ }^{\circ}\text{C}$  and mounted in

capillaries prior to determination. The data were consistent with the monoclinic space group  $P2_1/n$ . The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-square procedures. Semi-empirical absorption corrections were not required because there was less than 10% variation in the integrated  $\Psi$ -scan intensity data. The Si-N distances were restrained to an average N-Si distance of 1.74 Å. All non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atom on Al(1) was placed in an idealized position with the fixed Al-H distance of 1.50 Å. All other hydrogen atoms were treated as idealized contributions. The residuals for **2** are rather high due to marginal quality of the specimen. However, the metric parameters and their esd's around aluminum atoms appear to be of acceptable quality. The thermal ellipsoid diagram of **2** is shown in Figure 2. Details of the data collection for **1** and **2** are summarized in Table 1, and Table 2 shows selected bond distances and angles.

## Results and discussion

Bis(bis(trimethylsilyl)amino)alane  $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\mu\text{-H})\}_2$  (**1**) was obtained from disproportionation of the based-stabilized monomeric aminoalane  $[\text{H}_2\text{AlN}(\text{SiMe}_3)_2]\cdot\text{NMe}_3$  as described by idealized equation 1.<sup>3b</sup>



The anticipated formation of the alane trimethylamine byproduct,  $\text{H}_3\text{Al}\cdot\text{NMe}_3$ , would have been associated with its decomposition under toluene reflux conditions and precipitation of elemental aluminum,<sup>7</sup> which was indeed observed. We found this disproportionation

reaction to be crucially dependent on the substrate's concentration. For example, dilute toluene solutions did not show signs of the precipitation of elemental aluminum even after a several day-long reflux. On the other hand, appropriately concentrated solutions appeared to react as above in the course of several hours while intermediate removal of some toluene by evacuation accelerated the reaction's progress and resulted in increased yields. The isolation of **1**, after filtering out aluminum, was accomplished by low temperature recrystallization from hexane in which it was much less soluble than was unreacted  $[\text{H}_2\text{AlN}(\text{SiMe}_3)_2]\cdot\text{NMe}_3$ .

The characterization data acquired for **1** in this study were consistent with its chemical make-up as originally reported.<sup>3b</sup> Especially, the mass spectrum showed the parent ion for the dimer and other logically derived fragmentation ions. A few higher than dimer  $m/e$  fragments of extremely low intensity ( $< 1\%$ ) were also detected. This indicated that the dimeric association *via* H-bridges generally survived the heated probe and electron impact conditions in the MS experiment. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were in agreement with the original NMR data for **1** and, based on their simplicity, supported a symmetrical environment for the  $\text{N}(\text{SiMe}_3)_2$  groups while excluding a possible rigid, N-bonded structure.

The crystallographic determination for **1** provided two symmetry independent, but chemically similar, molecules in the asymmetric unit. Figure 1 shows the structure of one of the molecules. The molecule of **1** is a H-bridged dimer which is structurally very similar although not isomorphous with the H-bridged dimer bis(2,2,6,6-tetramethylpiperidino)alane,  $[\text{HAl}(\text{tmp})_2]_2$ ,<sup>2f</sup> or related F-bridged dimer  $[(\text{tmp})_2\text{AlF}]_2$ .<sup>8a</sup> For example, the wide average N–Al–N angle in **1**,  $124.6^\circ$ , can be compared with the same angles in  $[\text{HAl}(\text{tmp})_2]_2$ ,  $126.9(1)^\circ$  and  $[(\text{tmp})_2\text{AlF}]_2$ ,  $128.6(1)^\circ$ , and they all may reflect similar steric demands of the amino groups in these compounds. The environment around each N-atom in **1** is planar (2Si, N, and Al connected atoms lie in the same plane; sum of relevant angles is close to  $360^\circ$ ) and, although it is tempting to associate this

property with a mostly  $d_{\Pi}(\text{Si})-p_{\Pi}(\text{N})$  interaction in the  $\text{N}(\text{SiMe}_3)_2$  ligand, a planar environment appears to exist in the similar  $\{2\text{C}, \text{N}, \text{Al}\}$  fragment in  $[\text{HAl}(\text{tmp})_2]_2$  which is lacking such an interaction.

The average Al–N bond length in **1**, 1.824 Å, belongs to short distances of this type and its magnitude seems to be a consequence of a tetracoordinate Al atom bonded to a sterically congested tricoordinate N atom. This is strikingly supported by comparison with the Al–N distances in the relevant cases of the previously discussed  $[\text{HAl}(\text{tmp})_2]_2$ , 1.835(3) Å, and  $[(\text{tmp})_2\text{AlF}]_2$ , 1.832(2) Å, as well as of  $[\text{H}(\text{Cl})\text{AlN}(\text{SiMe}_3)_2]\cdot\text{NMe}_3$ ,<sup>4a</sup> 1.823(4) Å (for Al–N( $\text{SiMe}_3$ )<sub>2</sub>). Shorter Al–N distances are found in tricoordinate Al/tricoordinate N structures, for example, monomeric  $\text{Al}[\text{N}(\text{SiMe}_3)_2]_3$ , 1.78(2) Å,<sup>2g</sup> or six-membered planar ring  $[\text{MeAlN}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)]_3$ , 1.782(4) Å,<sup>8b</sup> but in the extremely congested monomeric  $t\text{-Bu}_2\text{AlN}(\text{SiPh}_3)_2$  this distance is 1.880(4) Å.<sup>8c</sup> On the other hand, in tetracoordinate Al/tetracoordinate N ring or cluster structures these lengths typically span the 1.9 to 2.0 Å range, for example, as in cubane  $(\text{PhAlNPh})_4$ , 1.914(5) Å,<sup>8d</sup> dimer  $[(\text{Me}_3\text{Si})_2\text{AlNH}_2]_2$ , 1.955 Å,<sup>8e</sup> and trimer  $(t\text{-Bu}_2\text{AlNH}_2)_3$ , 2.008 Å,<sup>8f</sup> although in the dimer  $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2\}_2$  this bond length is much shorter, 1.841 Å (av).<sup>8g</sup> These trends are illustrated by the structure of  $(\text{Me}_3\text{Si})_2\text{N}(\text{Me}_2\text{N})\text{Al}(\mu\text{-NMe}_2)_2\text{Al}(\text{H})\text{N}(\text{SiMe}_3)_2$  (**2**) (*vide infra*) that contains Al atoms connected to both tricoordinate N atoms (terminal congested  $\text{N}(\text{SiMe}_3)_2$  and noncongested  $\text{NMe}_2$ ) and tetracoordinate N atoms (bridging  $\text{NMe}_2$ ).

The Al–H distance of 1.727(1) Å in **1** is one of the longest among similar symmetrical Al–H bridging distances, possibly indicating a loose association of the monomers in the solid state. However, this can not be reconciled in a straightforward way with the dimer parent ion in the gas phase detected by mass spectrometry. This distance can be compared with the average Al–H lengths in the previously discussed symmetrical dimer  $[\text{HAl}(\text{tmp})_2]_2$ , 1.68 Å or trimer  $(t\text{-Bu}_2\text{AlH})_3$ , 1.726(5) Å.<sup>9a</sup> For the unsymmetrically H-bridged dimer of the  $[\text{H}_3\text{Al}\cdot\text{L}]_2$  type of alane adducts,

$[\text{H}_3\text{Al}\cdot\text{N}(\text{Me}_2)\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}]_2$ , the following Al–H distances are found that span almost the entire range of observable distances of this type, namely, two different ring distances, 1.84(3) Å and 1.99(5) Å, and two different terminal distances, 1.20(7) Å and 1.40(6) Å.<sup>9b</sup> Of particular interest also is the average Al–Al distance of 2.661 Å. It can be compared with this separation in other symmetrical dimers such as  $(\text{HAlMe}_2)_2$ , 2.62 Å<sup>9c</sup> and  $[\text{HAl}(\text{tmp})_2]_2$ , 2.680(2) Å. More importantly, this distance is in the range of the Al–Al bonding distances in structurally authenticated, neutral, monomeric dialanes  $[(\text{Me}_3\text{Si})_2\text{CH}]_4\text{Al}_2$ , 2.660(1) Å<sup>9d</sup> and  $[(i\text{-Pr}_3\text{C}_6\text{H}_2)]_4\text{Al}_2$ , 2.647(3) Å<sup>9e</sup> or tetrameric cluster  $[\text{Al}(\text{C}_5\text{Me}_5)]_4$ , 2.769 Å (av).<sup>9f</sup> Based on that, some bonding interaction along the Al–Al axis is thus probable in **1**.

A 1:1 ratio reaction of **1** and  $\text{HNMe}_2$  was performed to test preferences of the two possibly competing reactions, namely, aminolysis at the Al–H site with the formation of dihydrogen and transamination at the Al–N( $\text{SiMe}_3$ )<sub>2</sub> site(s) with the formation of  $\text{HN}(\text{SiMe}_3)_2$ . These types of reactions were observed to occur simultaneously in the combination of  $[\text{H}_2\text{AlN}(\text{SiMe}_3)_2]\cdot\text{NMe}_3$  and  $\text{NH}_3$ , and yielded a rare benzene soluble polymeric precursor that was used to make transparent AlN coatings on alumina substrates.<sup>3b</sup> Surprisingly, only minute quantities of  $\text{H}_2$  were measured several hours past addition indicating very slow aminolysis. This was further supported by an IR spectrum for raw products that showed a N–H stretching band at 3310  $\text{cm}^{-1}$  consistent with coordinated  $\text{HNMe}_2$  by **1** at this stage of reaction. The NMR spectra for the reaction mixture were run in the course of several weeks following addition and showed a multitude of slowly formed products. This was accompanied by increased quantities of evolved  $\text{H}_2$  (sharp  $^1\text{H}$  NMR resonance at  $\delta$  4.51<sup>10</sup>) and  $\text{HN}(\text{SiMe}_3)_2$  consistent with a relatively slow aminolysis and transamination in the system, respectively.

Compound **2** was isolated in small quantities after several days of a low temperature storage of the reaction mixture accompanied by a slow evaporation of volatiles. The NMR data obtained for a fresh solution of **2** in toluene- $d_8$  were complex and subject to changes

with time. These changes might be indicative of slow equilibration processes and formation of more stable symmetrical products in the solution but, also, of some on-going chemical interactions. Interestingly, the IR spectrum for the freshly isolated product showed only a single, well defined but, alas, broad band in the  $\nu(\text{Al-H})$  range at  $1860\text{ cm}^{-1}$ .

The molecular structure of **2** is shown in Figure 2. It features a puckered {Al-N-Al-N} ring with unsymmetrical (different) ligands on the aluminum atoms, and can be visualized as a  $\text{Me}_2\text{N}$ -bridged, two-site adduct of the different monomeric aminoalanes  $\text{Al}(\text{NMe}_2)_2[\text{N}(\text{SiMe}_3)_2]$  and  $\text{HAl}(\text{NMe}_2)[\text{N}(\text{SiMe}_3)_2]$ . The  $\text{N}(\text{SiMe}_3)_2$  groups on two different Al ring atoms are in the *cis* position to each other. Potentially increased steric congestion due to the *cis* configuration is apparently counterbalanced by ring puckering, which has the effect of moving apart the  $\text{N}(\text{SiMe}_3)_2$  groups on the congested side of the ring and getting the neighboring small H and  $\text{NMe}_2$  ligands closer on the other side of the ring with a concurrent decrease of the Al-Al distance. The latter distance of  $2.829(3)\text{ \AA}$  seems to be, however, outside the range of any significant aluminum-aluminum bonding interaction (*vide supra*). The ring puckering as defined by the angle between the  $\text{N}(1)\text{-Al}(1)\text{-N}(2)$  and  $\text{N}(1)\text{-Al}(2)\text{-N}(2)$  planes amounts to  $25.5^\circ$ . The N and Al atoms in the ring are four-coordinated; although the hydrogen atom is not resolved on Al(1), its presence is supported by both structural (pyramidal Al(1) atom) and chemical evidence (IR band in the  $\nu(\text{Al-H})$  range at  $1860\text{ cm}^{-1}$ ).

Despite the relatively high values of the residuals for **2**, the quality of the numerical data is good enough to address some of the molecule's structural aspects. The aluminum-nitrogen bonds in **2** represent a comprehensive range of bond configurations including ring and different exocyclic bonds, all in one molecule. The average Al-N distance in the ring (Al-*endo*- $\text{NMe}_2$ ),  $1.972\text{ \AA}$ , can be compared with the average distances of this type in some of the  $\text{Me}_2\text{N}$ -bridged dimers such as  $[\text{Al}(\text{NMe}_2)_3]_2$ ,  $1.965\text{ \AA}^{2e}$  (or  $1.970\text{ \AA}^{2d}$ ) and  $[\text{HAl}(\text{NMe}_2)_2]_2$ ,  $1.966\text{ \AA}^{2d}$  or trimer  $(\text{H}_2\text{AlNMe}_2)_3$ ,  $1.950\text{ \AA}^{2d}$ . The Al-*exo*- $\text{NMe}_2$  distance of  $1.782(8)\text{ \AA}$  in **2** belongs, in general, to very short Al-N bond lengths. For

example, the following Al-*exo*-NMe<sub>2</sub> distances are found in the dimers [Al(NMe<sub>2</sub>)<sub>3</sub>]<sub>2</sub>, 1.800 Å (av)<sup>2f</sup> (or 1.814 Å (av)<sup>2d</sup>), [HAl(NMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>, 1.804(2) Å,<sup>2d</sup> and [(Me<sub>2</sub>N)<sub>2</sub>Al{μ-N(H)1-Adamantany}]<sub>2</sub>, 1.793 Å<sup>2f</sup> while the apparently shortest to-date Al-N bond lengths are reported for monomeric Al[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, 1.78(2) Å,<sup>2g</sup> and six-membered planar ring [MeAlN(2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>]<sub>3</sub>, 1.782(4) Å.<sup>8b</sup> The other exocyclic AlN distance(s) in **2**, i.e. Al-*exo*-N(SiMe<sub>3</sub>)<sub>2</sub>, 1.839 Å (av), falls well within the range of similar terminal bonds. This is exemplified by comparison of this distance with the respective average lengths in **1**, 1.824 Å, {[ (Me<sub>3</sub>Si)<sub>2</sub>N ]<sub>2</sub> Al N H<sub>2</sub> }<sub>2</sub>, 1.841 Å,<sup>8g</sup> or {[ (Me<sub>3</sub>Si)<sub>2</sub>N ]<sub>2</sub> Al (NH<sub>2</sub>)<sub>2</sub> }<sub>3</sub> Al, 1.850 Å.<sup>8g</sup> The Al-*exo*-N(SiMe<sub>3</sub>)<sub>2</sub> lengths are generally longer than the Al-*exo*-NMe<sub>2</sub> lengths and this may reflect the congestion effect of the bulkier N(SiMe<sub>3</sub>)<sub>2</sub> group.

In summary, the structure of **2** illustrates the occurrence of both the aminolysis (absence of H on one of the Al atoms) and transamination (singular N(SiMe<sub>2</sub>)<sub>2</sub> groups on each Al atom) taking place in the reaction between **1** and HNMe<sub>2</sub>. Similar combinations of [H<sub>2</sub>AlN(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·NMe<sub>3</sub> and NH<sub>3</sub> were also reported to proceed *via* concerted ammonolysis and transamination and resulted in a soluble polymeric precursor to aluminum nitride.<sup>2b</sup> The data presented here are consistent with complex elimination chemistry in these systems and suggest that the new {[ (Me<sub>3</sub>Si)<sub>2</sub>N ]<sub>2</sub> Al (μ-H) }<sub>2</sub> may be a valuable precursor for conversion to aluminum nitride materials.

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**Table 1.** Crystallographic Data and Measurements for **1** and **2**.

	<b>1</b>	<b>2</b>
molecular formula	C <sub>24</sub> H <sub>74</sub> Al <sub>2</sub> N <sub>4</sub> Si <sub>8</sub>	C <sub>18</sub> H <sub>55</sub> Al <sub>2</sub> N <sub>5</sub> Si <sub>4</sub>
formula weight	697.55	507.99
crystal system	monoclinic	monoclinic
space group	P2 <sub>1</sub>	P2 <sub>1</sub> /n
a, Å	13.7119(2)	9.1715(5)
b, Å	18.3400(3)	22.9239(13)
c, Å	17.8971(4)	15.0291(9)
β, deg	91.4750(9)	96.088(2)
V, Å <sup>3</sup>	4499.20(18)	3139.9(3)
Z	4	4
μ, mm <sup>-1</sup>	0.297	0.260
temp, K	223(2)	198(2)
D <sub>calcd</sub> , g/cm <sup>3</sup>	1.030	1.075
crystal dimensions, mm	0.10 x 0.10 x 0.10	0.40 x 0.35 x 0.25
Θ range for data collection (deg)	1.14–28.21	1.63–22.50
no. of rflns collected	29387	7735
independent rflns	17056 (R <sub>int</sub> = 0.0584)	3809 (R <sub>int</sub> = 0.1028)
data/restraints/parameters	17056/9/697	3499/5/266
R (I > 2σ(I)); <sup>a</sup> wR2 <sup>b</sup>	0.0596; 0.1136	0.1220; 0.2918
R (all data); <sup>a</sup> wR2 <sup>b</sup>	0.1110; 0.1356	0.1708; 0.3411
goodness-of-fit <sup>c</sup>	1.027	0.975
final max/min Δρ, e/Å <sup>-3</sup>	0.320/–0.337	0.774/–0.923

$$^a R = \sum \Delta / \sum (F_o), \Delta = |F_o| - |F_c|; ^b wR2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [(wF_o^2)^2]^{1/2}$$

$$^c \text{GooF} = [\sum [w(|F_o| - |F_c|)^2] / (n - p)]^{1/2}$$

**Table 2.** Selected Bond Distances (Å) and Angles (°) for **1** and **2** with Estimated Standard Deviations in Parentheses

Bond Lengths			
<b>1</b>		<b>2</b>	
Al- <i>exo</i> -N (av)	1.824	Al(1)- <i>exo</i> -N(3)	1.836(4)
Al- <i>exo</i> -N; min/max	1.811(4)/1.844(4)	Al(2)- <i>exo</i> -N(5)	1.842(4)
		Al(2)- <i>exo</i> -N(4)	1.782(8)
		Al(1)- <i>endo</i> -N(2)	1.966(8)
		Al(1)- <i>endo</i> -N(1);	1.948(7)
		Al(2)- <i>endo</i> -N(1)	1.985(8)
		Al(2)- <i>endo</i> -N(2)	1.987(7)
Al- <i>endo</i> -H	1.727(1)	Al- <i>exo</i> -H (assumed)	1.50
Al-Al (av)	2.661	Al(1)-Al(2)	2.829(3)
Si-N (av)	1.755	Si-N (av)	1.743
Si-N; min/max	1.749(5)/1.765(5)	Si-N; min/max	1.7426(10)/1.7430(10)
Si-C (av)	1.874	Si-C (av)	1.87
Si-C; min/max	1.850(7)/1.900(6)	Si-C; min/max	1.834(14)/1.889(10)
Bond Angles			
<b>1</b>		<b>2</b>	
N-Al-N (av)	124.6	N(1)-Al(1)-N(2)	86.1(3)
N-Al-N; min/max	124.2(2)/125.1(2)	N(1)-Al(2)-N(2)	84.5(3)
N-Al-Al (av)	117.7	Al(1)-N(1)-Al(2)	92.0(3)
N-Al-Al; min/max	115.19(14)/120.5(2)	Al(1)-N(2)-Al(2)	91.4(3)
Si(2)-N(1)-Al(1)	115.0(2)	N(3)-Al(1)-N(1)	116.4(3)
Si(1)-N(1)-Al(1)	125.9(3)	N(3)-Al(1)-N(2)	122.4(3)
Si(2)-N(1)-Si(1)	118.7(2)	N(4)-Al(2)-N(5)	111.3(3)

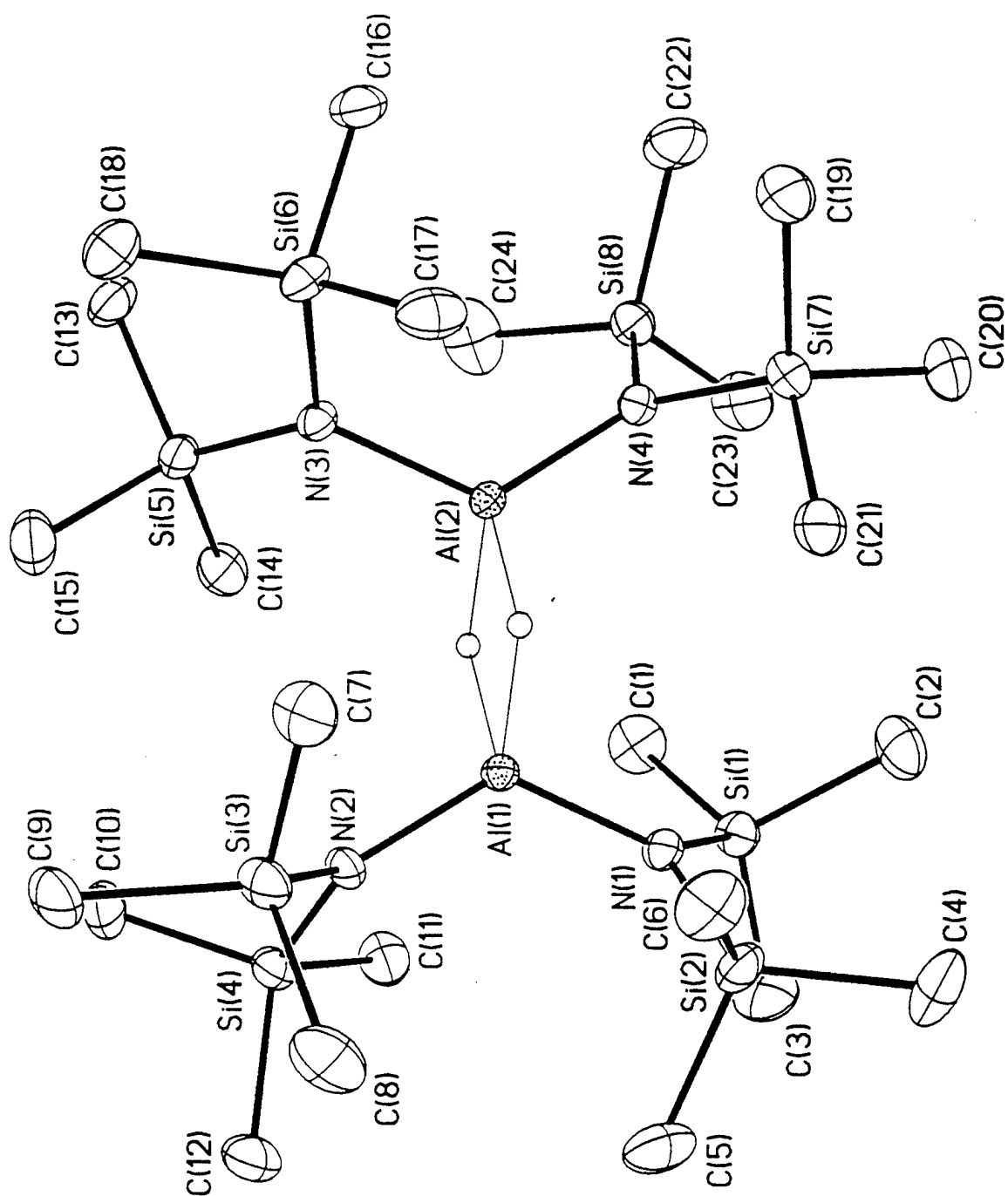
**Table 2, continued**

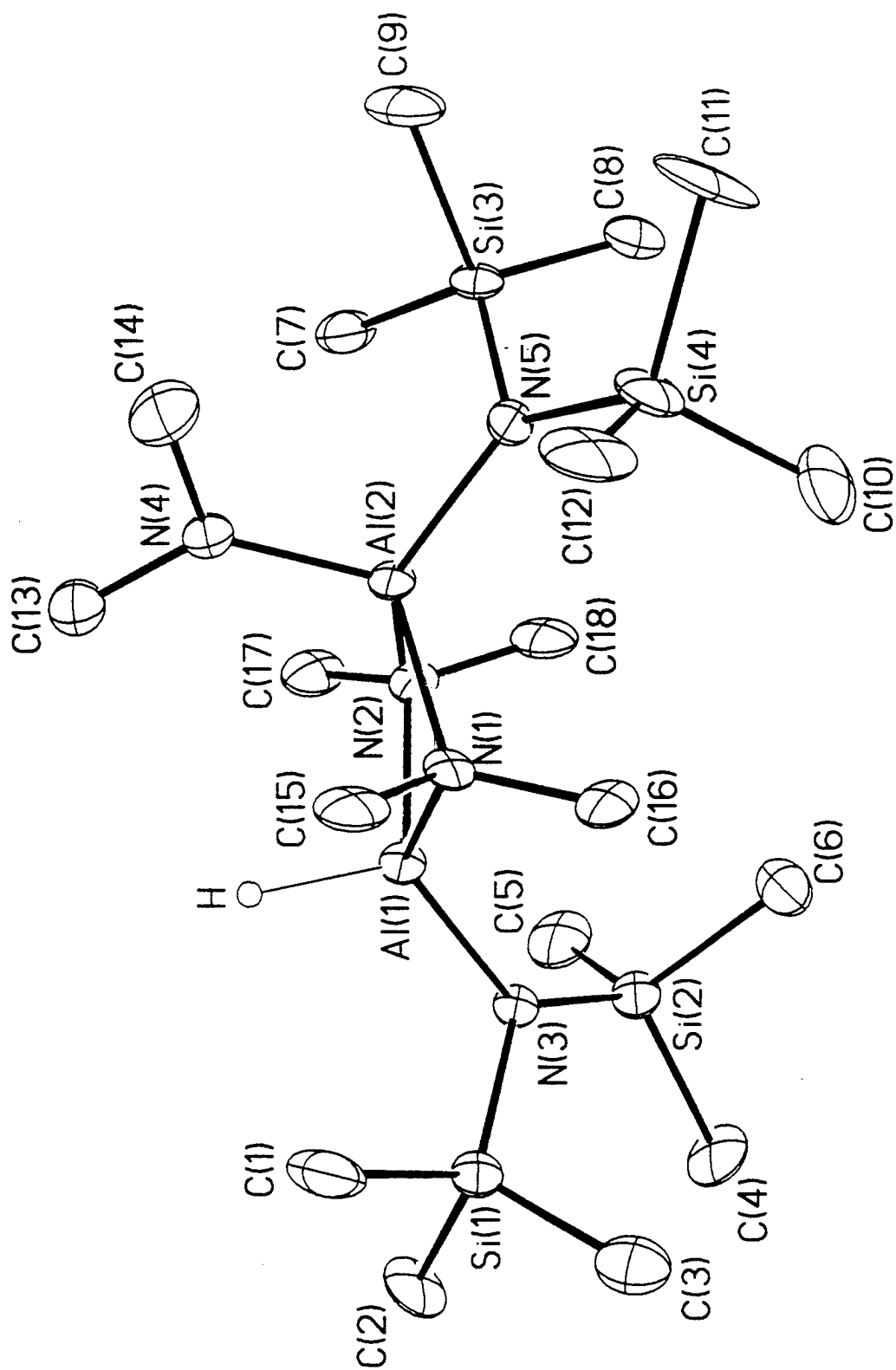
Bond Angles		
1	2	
	N(4)–Al(2)–N(1)	110.2(4)
	N(4)–Al(2)–N(2)	114.0(4)
	N(5)–Al(2)–N(2)	114.9(4)
	N(5)–Al(2)–N(1)	119.5(3)

## Captions for Figures

**Figure 1.** Thermal ellipsoid diagram (30% probability ellipsoids) showing the molecular structure of **1** (independent molecule 1). All C-hydrogen atoms are omitted for clarity.

**Figure 2.** Thermal ellipsoid diagram (30% probability ellipsoids) showing the molecular structure of **2**. All C-hydrogen atoms are omitted for clarity.





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